



Preparation and characterization of aluminium – containing MCM-41

Griselda A. Eimer^a, Liliana B. Pierella^a, Gustavo A. Monti^b,
Oscar A. Anunziata^{a,*}

^a *Grupo de Fisicoquímica de Nuevos Materiales – CITEQ (Centro de Investigación y Tecnología Química), Facultad Regional Córdoba, Universidad Tecnológica Nacional, CC36 – Suc. 16, Córdoba 5016, Argentina*

^b *Facultad de Matemática, Astronomía y Física, Universidad Nacional de Córdoba, LANAIS RMS (Fa.M.A.F., UNC-CONICET), Córdoba 5000, Argentina*

Received 30 July 2002; received in revised form 14 January 2003; accepted 19 January 2003

Abstract

Mesoporous aluminosilicate molecular sieves with the MCM-41 structure ($\text{Si}/\text{Al} = 20$) have been synthesized using tetraethoxysilane (TEOS) and sodium aluminate (NaAlO_2) as Si and Al sources and hexadecyltrimethylammonium bromide (HTMABr) and varying several parameters during the preparation process. All the samples were characterized by X-ray diffraction (XRD), Fourier transformed infrared (FT-IR) and solid state MAS NMR spectroscopy. A significant improvement in the structure by using a novel method for template removal has been evaluated.

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Keywords: Al-MCM-41; Mesoporous materials; M41S; Nanostructured materials; Synthesis; Characterization

1. Introduction

The preparation and engineering of porous silicate materials is an area of intense scientific and technological activity. Mesoporous molecular sieves of the MCM-41 type possess a hexagonal packed array of channels with narrow pore size distributions. Since the first report of the structure in 1992 [1,2], a number of studies have been

performed aiming to modify the MCM-41 synthesis procedure in order to increase the potential applicability of these materials [3]. Interesting physical properties of these materials include a regular pore structure and pore shape, a highly specific surface of up to $1000 \text{ m}^2/\text{g}$, a specific pore volume of up to 1.3 ml/g and a high thermal stability. These properties allow such materials a strong potential for application in heterogeneous catalysis, supramolecular assembly, separation, biomedicine and encapsulation [4–7]. The regular system of large channels in MCM-41 hosts offers unique opportunities for the preparation of new nanostructure composite materials. As relentless efforts continue to reduce the size of electronic

* Corresponding author. Tel.: +54-351-469-0585; fax: +54-351-469-0585.

E-mail address: [oanunziata@scdt.frc.utn.edu.ar](mailto: oanunziata@scdt.frc.utn.edu.ar) (O.A. Anunziata).

circuitry to reach higher storage density and faster processing speed, new concepts are being developed to build electronic circuits from molecular components. In this way, the encapsulation of nanosized conducting polymer filaments, semiconductors, and metals into the channels of MCM-41, would permit the feasibility of using mesoporous materials as nanometer-scale electronic devices [7–10]. MCM-41 is prepared generally by hydrothermal reactions of aluminosilicate or silicate gels in the presence of quaternary ammonium surfactants in the temperature range from 100 to 200 °C [1,2]. There are many reports of synthesis and characterization of Al-MCM-41 with different Si/Al ratios and with different alumina or silica sources, prepared by adding aluminium sources prior to calcination [1,2,11–19]. A variety of silica sources have been reported, including sodium silicate and silicon alkoxides and the most often-used aluminium sources are sodium aluminates, aluminium sulfate, aluminium nitrate and aluminium isopropoxide. In our previous works, we reported a novel route to prepare aluminosilicates Al-MCM-41 and Al-MCM-48 with both well-defined morphology and high structural ordering, using tetraethoxysilane (TEOS) and sodium aluminate (NaAlO_2) as silica and aluminium sources, respectively [20,21]. In the present work, we studied the influence of the surfactant/Si molar ratio and synthesis time with regard to changes in structural features of Al-MCM-41 synthesized with hexadecyltrimethylammonium bromide (HTMABr) as template. Moreover, the effect of the thermal process for template removal on structural stability and order, reticular contraction and mesoporous framework composition have been discussed.

2. Experimental

The Al-MCM-41 mesoporous material was prepared as follows: Firstly, TEOS (Aldrich, 98%) and NaAlO_2 (Johnson Matthey) were vigorously mixed for 30 min. Then, a 10 wt% solution of HTMABr (Aldrich, 99%) in ethanol was added drop wise under stirring at room temper-

ature. Tetraethylammonium hydroxide 20 wt% aqueous solution (TEAOH) (Merck) was added to the resultant solution and stirring was continued during 5 h. Then, TEAOH and water were further dripped into the milky solution. The mixture was heated at 80 °C for 30 min to remove ethanol used in solution and produced in the hydrolysis of TEOS. The pH of the resultant gel was 11.5. This gel was heated in a static Teflon-covered reactor under autogenous pressure at 100 °C during 0–10 days. The final solid reaction product was extracted from the autoclave, filtered, washed with distilled water and dried at 60 °C overnight (as-synthesized MCM-41). The molar composition of the gels subjected to hydrothermal synthesis was as follows: Si/Al = 20, TEAOH/Si = 0.3, surfactant/Si = 0.1–0.45, water/Si = 60. The post-synthesis thermal treatment evaluated to remove the template was: temperature-programmed-desorption (TPD) (heating rate of 1 °C/min under N_2 flow of 5 ml/min) to 500 °C maintaining this temperature for 6 h and further temperature-programmed calcination (heating rate of 1 °C/min under air flow of 5 ml/min) to 500 °C maintaining also this temperature for 6 h. For the studies of temperature-programmation was employed an INSTRELEC programmer, which admits to change the heat slope. The sodium form of the Al-MCM-41 was characterized by X-ray diffraction (XRD), Fourier transformed infrared (FT-IR) and solid state MAS NMR spectroscopy. X-ray powder diffraction patterns were collected in air at room temperature on a Rigaku diffractometer using CuK_α radiation of wavelength 0.15418 nm. Diffraction data were recorded between $2\theta = 1$ and 10° at an interval of 0.01° . A scanning speed of 2° per minute was used. The repetition distance of the pores “ d ” was obtained by the Bragg law using the position of the first XRD line. The lattice parameter “ a_0 ” of the hexagonal unit cell was calculated from the equation $a_0 = (2/\sqrt{3})d_{100}$. The pore diameter may be calculated from this value by subtracting 1.0 nm, which is an approximate value for the pore wall thickness usually found in MCM-41 synthesized in a similar procedure. Infrared spectra of the samples were recorded on a JASCO 5300 FT-IR spectrometer either on KBr pellets or on

self-supported wafers. The FT-IR spectra in the lattice vibration region were performed using KBr 0.05% wafer technique. Solid state NMR spectra were taken on a BRUKER MSL300 spectrometer operating at 78.2 MHz for ^{27}Al . We used a commercial (BRUKER) MAS 300WB CP1H-BBWH. VTN-BL4 probe with 4 mm o.d. zirconia rotors. The sample was spun at the magic angle at a rate of 5 kHz. Experiments were carried out at ambient probe temperature (ca. 297 K). The ^{27}Al spectrum was recorded using direct polarization with pulses of 2 μs duration and a relaxation delay of 2 s. Aluminium chemical shifts are quoted with respect to 1 M aluminium nitrate.

3. Results and discussion

3.1. Influence of surfactant/Si ratio

It is well known that the surfactant/Si ratio is a critical variable in the formation of liquid-crystal template M41S materials. The XRD patterns of the calcined samples at various surfactant/Si ratios are presented in Fig. 1. Such patterns were fitted with an error (R^2) = 0.9867 using a mathematical soft called Origin 6.0. For a, b and c samples a sharp peak ascribed to the (100) reflection of the hexagonal structure of the mesopores was observed at $2\theta = 1.99\text{--}2.08^\circ$ corresponding to $a_0 = 4.9\text{--}5.1$ nm. Besides the strong peak, curve-fitting calculations allowed us to discriminate weak ones ascribed to (110) and (200) reflections at $2\theta = 3.66^\circ$ and 4.20° , respectively, characteristic of hexagonal ordering. However, the samples exhibited differences in their peak intensities and widths. The normalized (100) peak intensity increased in the order $a < b < c$ while its width increased in the reverse order $c < b < a$. This reflects an increase in structural order from sample a to sample c which is according to the enhanced surfactant concentration [22]. Furthermore the structure was transformed from hexagonal into cubic upon increasing the surfactant/Si ratio to 0.45 (sample d), in agreement with the effect of concentration on the formation of a liquid-crystal phase for the

HTMABr system [23,24]. With the increasing surfactant concentration, the liquid-crystal structure of the lyotropic surfactants such as HTMA and DTMA (dodecyltrimethylammonium) changes from hexagonal into cubic, and finally into lamellar [24].

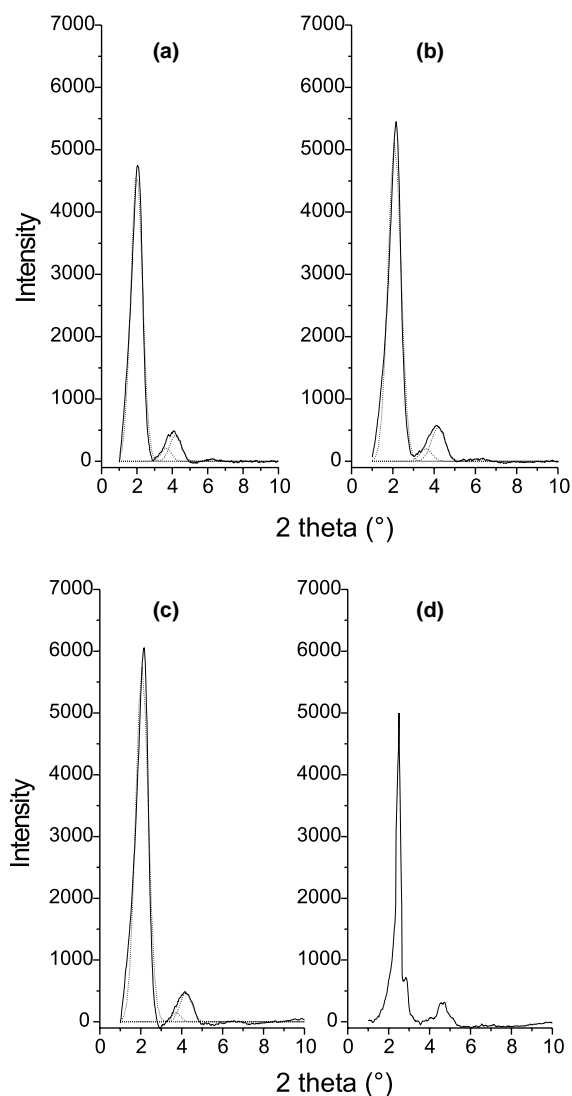


Fig. 1. XRDs patterns of calcined Al-MCM-41 with surfactant/Si molar ratio: (a) 0.1, (b) 0.2, (c) 0.3, (d) 0.45. Hydrothermal synthesis conditions: 100 $^\circ\text{C}$, 10 days, static (—, experimental; ---, fitted).

3.2. Influence of synthesis time

Fig. 2 shows the degree of ordering of the pore structure (structural regularity) of Al-MCM-41 samples with surfactant/Si ratio = 0.2, as a function of reaction time. The ordering degree of the structure was evaluated against an *internal standard* sample (hydrothermal treatment for 10 days) which was arbitrarily considered as *reference* (100% of regularity) as it showed the better-defined XRD pattern with the highest intensity for the (100) diffraction peak. As shown in Fig. 2, mesostructure was formed even before the hydrothermal treatment. The regularity of the products increased with the synthesis time and was maximum after 10 days. However, a hydrothermal treatment during 5 days is appropriate to synthesize Al-MCM-41 with a suitable structure order in the present reaction conditions (Si/Al = 20, Si and Al sources: TEOS and NaAlO₂, respectively, surfactant: HTMABr). The XRD pattern of samples obtained with short hydrothermal treatments was not defined enough to discriminate the hexagonal structure from the lamellar one. However, it is well known that the lamellar phase is decomposed when it is calcined [1] and all our samples were stable on calcination at 500 °C.

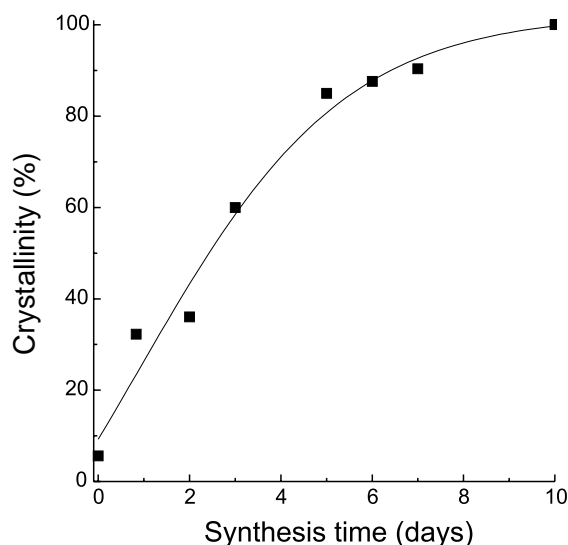


Fig. 2. Effect of synthesis time on the degree of Al-MCM-41 structural ordering. Surfactant/Si molar ratio = 0.2. Hydrothermal synthesis conditions: 100 °C, 0–10 days, static.

3.3. Influence of post-synthesis treatment

Fig. 3 shows the XRD patterns for the Al-MCM-41 sample (surfactant/Si ratio = 0.2 and 10 days of synthesis time), “as-synthesized” and after post-synthesis thermal treatment for template removal. As can be seen, the (100) Bragg reflection increases sharply in intensity upon removal of the hexadecyltrimethylammonium ion template in contrast with the results reported by other authors who observed that after calcination the intensity of the diffraction peaks decreases [16]. On calcination of as-synthesized mesoporous materials, a lattice contraction is commonly observed due to the removal of the surfactant template from the channels and in agreement with the condensation of silanol (SiOH) groups in the walls. As reported by us elsewhere [20], the template removal using hexadecyltrimethylammonium – thermal – programmed desorption under N₂ flow and subsequent thermal-programmed calcination under air flow produced minor lattice contractions in the mesostructure framework and long-range ordered structure.

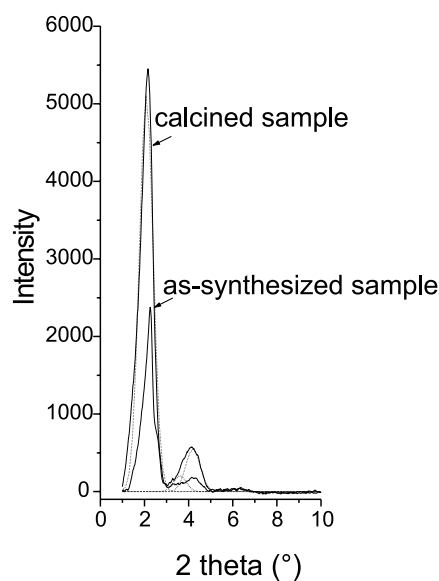


Fig. 3. Change of XRD pattern with post-synthesis thermal treatment of as-synthesized Al-MCM-41. Surfactant/Si molar ratio = 0.2. Hydrothermal synthesis conditions: 100 °C, 10 days, static.

Table 1
Frequencies (cm^{-1}) and suggested band assignment of the Al-MCM-41 framework

Samples	Asym. stretching		Terminal Si-O ⁻	Sym. stretching	T-O bending
	External	Internal			
Calcined sample	1228 (w)	1082 (s)	962 (m)	802 (m)	460 (s)
As-synthesized sample	1223 (m)	1060 (s)	964 (m)	790 (m)	449 (s)

w, Weak; m, medium; s, strong.

The detailed frequencies of the main IR absorption bands of the Al-MCM-41 sample with surfactant/Si ratio = 0.2 and hydrothermally treated for 10 days, together with a qualitative indication of their relative intensities and suggested assignments are given in Table 1. The absorption bands at 1060 and 1223 cm^{-1} in the as-synthesized sample are due to internal and external asymmetric Si-O stretching modes. They are shifted to higher frequencies (1082 and 1228 cm^{-1} , respectively) in the calcined sample. The bands at 790 and 449 cm^{-1} (in the as-synthesized sample) are assigned to symmetric Si-O stretching and tetrahedral Si-O bending modes, respectively, and also are slightly shifted to higher frequencies upon calcination. Such positive shifts in frequencies would reflect the formation of new Si-O-Si and Si-O-Al bridges during calcinations. In this way, it is probably due to an increased network cross-linking [25], and would account for the lattice contraction and structural stabilization that Al-MCM-41 undergoes upon template removal and calcination process. Furthermore, the sample exhibited a band at 962–964 cm^{-1} , which could be assigned to the stretching vibration of Si-O⁻ groups [26–29].

Fig. 4 shows the ²⁷Al solid-state MAS-NMR spectra of the Al-MCM-41 sample (surfactant/Si ratio = 0.2 and 10 days of synthesis time), “as-synthesized” and after post-synthesis thermal treatment. The spectra exhibit two peaks with shifts of 53 ± 2 and 0 ± 2 ppm. The signal at 53 ± 2 ppm is assigned to tetrahedrally coordinated framework aluminium (T_d-Al) [30]. The signal at 0 ± 2 ppm is assigned to octahedral coordinated (O_h-Al) non-framework aluminium [30]. As it can be observed, aluminium was incorporated mainly with tetrahedral coordination in the framework of MCM-41, prepared by the present

synthesis procedure. After post-synthesis thermal treatment the signal due to the symmetrical octahedral Al nuclei is significantly reduced leaving a strong intensity signal due symmetrical 4-coordinate Al. This result indicates thermally induced co-condensation of Al species into the silica lattice during the post-synthesis thermal process, along with the removal of water of hydration from surface Al species that previously possessed O_h coordination [15]. This feature is in contrast with the results of various authors who reported that the appearance of octahedral coordinated extra-framework aluminium species is due to its intrinsic formation during hydrothermal crystallization and/or by dealumination during calcination of the as-synthesized Al-MCM-41 [12,14,16,17]. Thus, ²⁷Al NMR data of our samples suggest that the

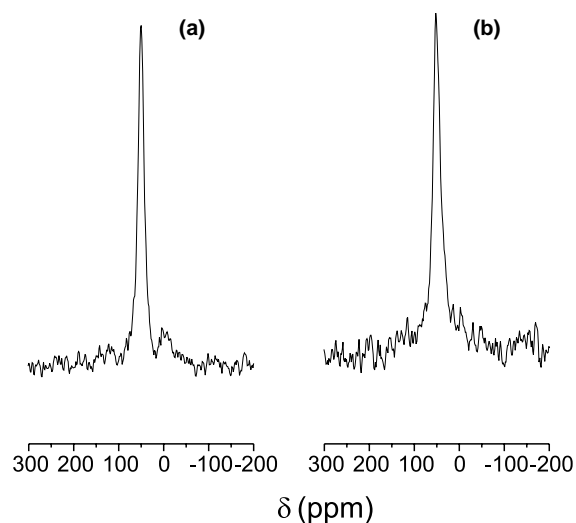


Fig. 4. ²⁷Al solid-state MAS NMR spectra of the Al-MCM-41 samples: (a) as-synthesized, (b) after post-synthesis thermal treatment. Surfactant/Si ratio = 0.2. Hydrothermal synthesis conditions: 100 °C, 10 days, static.

thermal-programmed post-synthesis treatment favours the introduction of Al in the tetrahedral framework position.

Presently, we are studying different methods for the encapsulation of polyaniline filaments into the channels system of Al-MCM-41 materials synthesized by us.

4. Conclusions

Al-MCM-41 mesoporous materials with a Si/Al ratio of 20 were prepared by hydrothermal synthesis using NaAlO₂ and TEOS as aluminium and silica sources, respectively, and HTMABr as template. This route of synthesis provided mesoporous materials with high structural regularity and tetrahedrally coordinated Al into the silica framework. These features were maximized by a suitable temperature protocol and by the nature of the gas atmosphere (first N₂ and then O₂) employed in the removal process of the template. Upon calcination, all the products showed a better-defined framework as inferred from their more intense and better-resolved peaks in its XRD pattern after calcinations. The structural ordering increased with increasing synthesis time and surfactant/Si ratio. FT-IR studies allowed us to obtain information about the mesostructure framework before and after template removal.

Acknowledgements

Conicet Reserchers: O.A.A., L.B.P., G.A.M. and G.A.E; The authors are grateful to Agencia Córdoba Ciencia of Argentina for financial support, Tri-anual Project No. 161/01.

References

- [1] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, *Nature* 359 (1992) 710.
- [2] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, *J. Am. Chem. Soc.* 114 (1992) 10834.
- [3] A. Corma, *Chem. Rev.* 97 (1997) 2373.
- [4] H. Koch, W. Reschetilowski, *Microporous Mesoporous Mater.* 25 (1998) 127.
- [5] R. Hoppe, A. Ortlam, J. Rathousky, G. Schulz, E. Zukel, *Microporous Mater.* 8 (1997) 267.
- [6] E. Chomski, O. Dag, A. Kuperman, N. Coombs, G. Ozin, *Chem. Vap. Deposition* 2 (1) (1996) 8.
- [7] C.-G. Wu, T. Bein, *Science* 264 (1994) 1756.
- [8] K. Moller, T. Bein, *Chem. Mater.* 10 (1998) 2950.
- [9] C.-G. Wu, T. Bein, *Science* 266 (1994) 1013.
- [10] C.-G. Wu, T. Bein, *Chem. Mater.* 6 (1994) 1109.
- [11] A. Monnier, F. Schuth, Q. Huo, D. Kumar, D. Margolese, R.S. Maxwell, G.D. Stucky, M. Krishnamurty, P. Petroff, A. Firouzi, M. Janicke, B.F. Chmelka, *Science* 261 (1993) 1299.
- [12] R. Schmidt, D. Akporiaye, M. Stocker, O.H. Ellestad, *J. Chem. Soc., Chem. Commun.* (1994) 1493.
- [13] Y. Sun, Y. Yue, Z. Gao, *Appl. Catal. A: General* 161 (1997) 121.
- [14] H. Kosslick, G. Lischke, B. Paelitz, W. Storek, R. Fricke, *Appl. Catal. A: General* 184 (1999) 49.
- [15] S.A. Bagshaw, F. Testa, *Microporous Mesoporous Mater.* 39 (2000) 67.
- [16] Y. Cesteros, G.L. Haller, *Microporous Mesoporous Mater.* 43 (2001) 171.
- [17] B. Lindlar, A. Kogelbauer, R. Prins, *Microporous Mesoporous Mater.* 38 (2000) 167.
- [18] B. Chakraborty, B. Viswanathan, *Catal. Today* 49 (1999) 253.
- [19] I. Diaz, F. Mohino, J. Perez-Pariente, E. Sastre, *Appl. Catal. A: General* 205 (2001) 19.
- [20] G.A. Eimer, L.B. Pierella, G.A. Monti, O.A. Anunziata, *Catal. Lett.* 78 (1–4) (2002) 65.
- [21] G.A. Eimer, L.B. Pierella, O.A. Anunziata, *Studies in Surface Science and Catalysis Version 06-P-08*, 2001, p. 135.
- [22] K.A. Koyano, T. Tatsumi, *Microporous Mater.* 10 (1997) 259.
- [23] K.A. Koyano, T. Tatsumi, *Chem. Commun.* (1996) 145.
- [24] P.K. Vinson, J.R. Bellare, H.T. Davis, W.G. Miller, L.E. Scriven, *J. Colloid Interface Sci.* 142 (1991) 74.
- [25] M.V. Landau, S.P. Varkey, M. Herskowitz, O. Regev, S. Pevzner, T. Sen, Z. Luz, *Microporous Mesoporous Mater.* 33 (1999) 149.
- [26] J. Perez Pariente, J. Sanz, V. Fornes, A. Corma, *J. Catal.* 124 (1990) 217.
- [27] M.A. Camblor, A. Corma, J. Perez Pariente, *J. Chem. Soc., Chem. Commun.* (1993) 557.
- [28] M.A. Camblor, M. Constantini, A. Corma, L. Gilbert, P. Esteve, A. Martinez, S. Valencia, *J. Chem. Soc., Chem. Commun.* (1996) 1339.
- [29] S. Dzwigaj, P. Massiani, A. Davidson, M. Che, *J. Mol. Catal. A: Chemical* 155 (2000) 169.
- [30] G. Engelhardt, *Stud. Surf. Sci. Catal.* 58 (1991) 285.